Direct Imaging of Surface Reconstructions on CdTe by High-Resolution Electron Microscopy

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We report direct observations of surface reconstructions on CdTe by high-resolution electron microscopy in the profile-imaging geometry. The predominant surface was (111) which was often found to be twinned. Image simulations confirmed that the (110) reconstruction was similar to that derived from low-energy electron diffraction studies. A metastable $3\times n$ reconstruction was observed on the (100) surface.

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An accurate description of the atomic geometry of single-crystal surfaces is important for understanding surface chemistry and gas-solid and solid-solid interactions. In the case of semiconductors, these geometries also govern the nature of electronic surface states as well as affecting the initial stages of epitaxial growth. Traditional diffraction and spectroscopic techniques such as low-energy electron diffraction (LEED) and Auger-electron spectroscopy provide information averaged over comparatively large areas of surface. On the other hand, localized real-space information about surface steps, terraces, domains, and defects can be obtained with high-resolution electron microscopy, particularly in the profile-imaging geometry.[1-3] In this Letter we first present profile images of CdTe showing the different types of reconstruction which occur on (110), (111), and (100) surfaces. We then discuss our results for (110) surfaces in more detail, using image simulations and a structural model derived from LEED.[4]

Cadmium telluride (CdTe) is an interesting semiconductor compound with electronic properties which make it suitable for solar-cell applications. Atomic motion at CdTe surfaces was observed in profile[5] but surface reconstruction was not reported, possibly because the available microscope resolution was limited to about 3 Å or perhaps the surfaces studied were not completely clean. In our present study we have used a JEM-4000EX high-resolution electron microscope, operated at an accelerating voltage of 400 kV, which had demonstrated an interpretable resolution of better than 1.7 Å.[6] Our samples were prepared by crushing with an agate mortar and pestle under purified methanol followed by placing of a drop of the resulting suspension on a holey carbon support film. In an attempt to avoid, or at least minimize, surface contamination, the specimens were immediately transferred to the microscope air lock where they were dried out during the pump-down process. This procedure did not, however, always lead to a completely clean surface—a thin amorphous layer of perhaps 3–5 Å often still covered the surface. Clean surfaces could always be obtained by our first removing the condenser aperture with the beam crossover located above the sam-

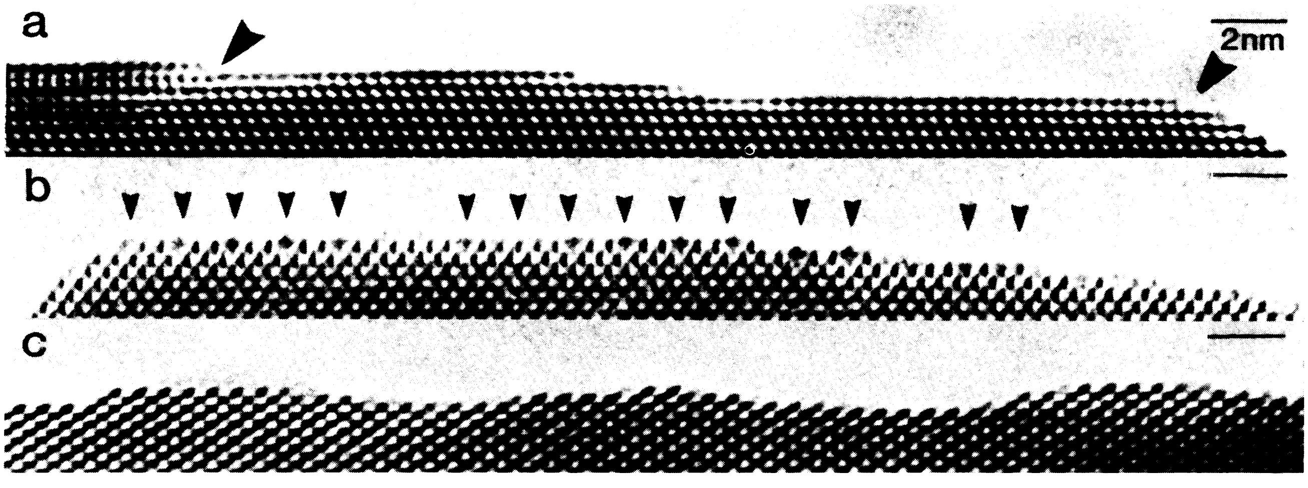

FIG. 1. Profile images for CdTe, in [1$\bar{1}$0] projection, showing (a) (111) surface with twinning, (b) $\times 3$ reconstruction on (001) surface, and (c) (1×1) reconstruction on (110) surface.

ple, and then gradually converging the illumination until parts of the CdTe crystal actually sublimed away from the surface. Comparatively large surface rearrangements took place on crystals treated in this manner[7]; moreover, the $\times 3$ reconstruction of the (100) surface was only seen on these crystals. Despite the vacuum level of 10^{-7} Torr in the microscope column, it was interesting that the surface reconstructions would often remain for lengthy periods (~ 1 h or more), provided only that surface reactions induced by high electron irradiation levels did not occur.

The CdTe crystals have been observed in the $\langle 110 \rangle$ projection since this direction is unique in providing (111), (100), and (110) surface profiles. The crystals have generally been dominated by (111) surfaces which are long and flat. Comparatively few (110) and (100) surfaces were observed and these were usually very short and stepped, as might be expected since (111) surfaces have lower surface energy than the (110) and (100) surfaces. As is clearly visible in Fig. 1(a), many of the (111) surfaces ($\simeq 50\%$–60%) were found to have the surface layer, or layers, of atoms in a twinned relationship with respect to the bulk crystal (each extended black spot in the image corresponds to a CdTe pair of atoms in this projection). In general, there was nothing distinctive about the (100) surface as observed along [110] but, as shown in Fig. 1(b), a $\times 3$ periodicity was observed in the case of the crystals which had been intensively heated with the electron beam. This $\times 3$ reconstruction, which could be analogous to the 3×1 reconstruction seen on GaAs(100) surfaces,[8,9] was not very stable under electron irradiation and considerable atomic motion on this surface could be observed with the television image-pickup system attached to the microscope. Finally, Fig. 1(c) is an image of the (110) surface which suggests that the outermost columns of Cd-Te dimers are rotated relative to their orientations in the bulk material. This characteristic "chevron" appearance is expected from structural models of a reconstructed (110) surface.[4]

Our initial objective was to study the CdTe(110) surface since the nature of reconstructed (110) surfaces of many compound semiconductors had already been characterized by LEED.[10] In general, the reconstruction consists of a slight average movement (contraction) of the outermost (surface) dimers towards the bulk accompanied by a rotation of the dimer, with the cation contracted further inward and the anion relaxed outward. In the case of CdTe, LEED studies[4] indicate a (0.05 ± 0.05)-Å contraction and a rotation angle $w = 30.5°$. Figure 2 shows the schematic model for this reconstruction, in profile view, which was used as a basis for computer calculations.

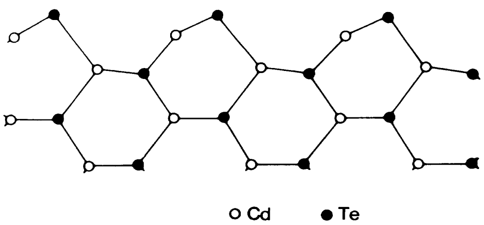

FIG. 2. Schematic model for reconstruction of (110) surface of CdTe as viewed in profile along the $[1\bar{1}0]$ projection (after Ref. 4).

The image simulations used a modified version of the multislice programs of Ishizuka, taking as input the atomic coordinates due to Duke *et al.*[4] and the operating parameters of the JEM-4000EX.[6] Figure 3 shows a through-focal series of calculations for CdTe(110) surfaces with, and without, reconstruction at crystal thicknesses of 45.8 and 91.6 Å. The difference in appearance of the two surfaces is distinct, particularly at the so-called "white-dot" focus (-1150 Å) where the contrast at the atom-pair positions is white.

In practice, it was found that *all* of the (110) surfaces observed were reconstructed *if* they were clean, which was an important result given the comparatively poor vacuum (at least in surface science terms). The reconstruction was generally quite stable with respect to experimental conditions and took place over distances as short as three or four unit cells. Figure 4 shows two high-magnification electron micrographs recorded as part of a focal series, together with matching image simulations. The first pair of images corresponds to black spots at the atom-pair positions while the last pair is at the white-spot contrast position. We are currently in the process of trying to quantify the extent of the reconstruction directly from the micrographs, in particular to evaluate how accurately the rotation angle might be measured.

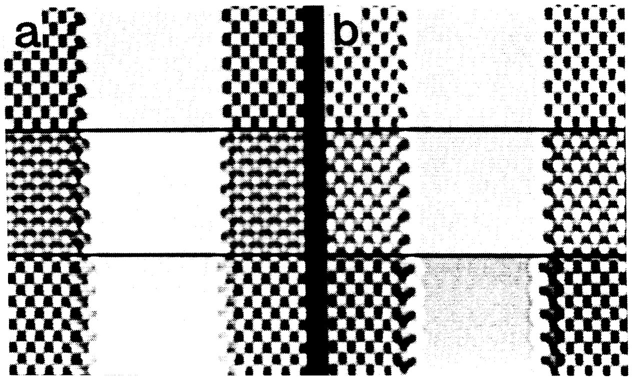

FIG. 3. Simulated 400-keV profile images for CdTe, in $[1\bar{1}0]$ projection, showing the (110) surface with (left edge) and without (right edge) surface reconstruction. (a) Thickness $= 45.8$ Å. (b) Thickness $= 91.6$ Å. Defocus values from top to bottom are -450, -750, and -1150 Å.

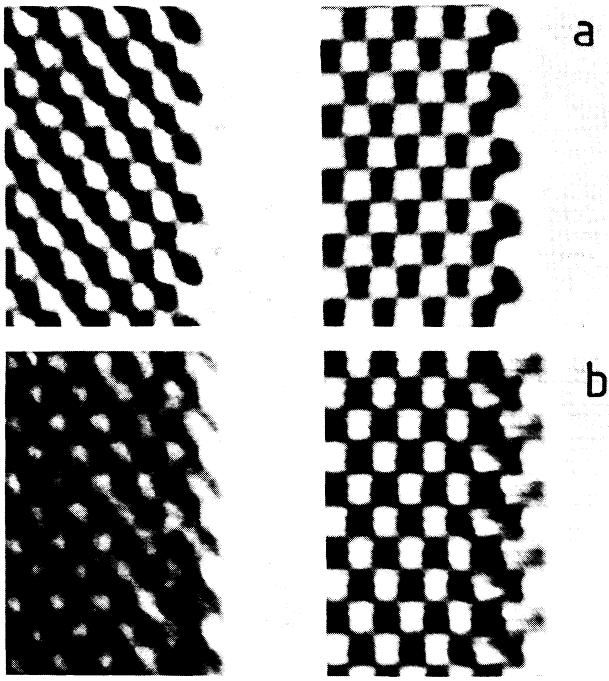

FIG. 4. Experimental (left) and simulated (right) images for CdTe, in [1$\bar{1}$0] projection, showing the reconstructed (110) surface: (a) "black-spot contrast," −450 Å, and (b) "white-spot contrast," −1150 Å.

Cadmium telluride is a highly ionic compound, having a large shear (30.5°) reconstruction on its (110) surface which is similar to the reconstructions on GaAs(110) and InSb(110), whose bonding is very convalent, and yet different from the reconstructions on (1120) and (1010) surfaces of ZnO and MgO(100) whose bonding is ionic.[10] This was a surprising result when the structural models for the reconstructions were first proposed since any correlation between bonding ionicity and the magnitude and type of layer reconstruction was eliminated. Although we have not yet determined the polarity of the surface by an independent means, our experimental images and matching simulations tend to support this large relaxation model.

The results[11] from LEED for III-V compounds (GaAs,InSb,InP) show that the reconstructions on their (110) surfaces are independent of specimen preparation technique and the thermal history of the surface. The intensity-voltage curve profiles for strongly anion-deficient (110) surfaces are identical to those measured from stoichiometric surfaces. This latter result can only be explained by the assumption that identical reconstructions occur on small stoichiometric surfaces and that any excess cations actually form metallic clusters. We found the (110) reconstruction to be stable relative to experimental conditions and that it can take place over dimensions as short as a few unit cells. Our results for CdTe suggest that there is a similar rule governing the (110) surface reconstructions of CdTe as for these other compounds. It will be interesting to investigate whether other covalent-bonded surfaces will retain their reconstructions under what would normally be considered as unclean conditions.

In summary, we have directly observed the first high-resolution profile images of clean cadmium telluride surfaces which show clear evidence for different types of reconstruction on different surfaces. The good agreement between experimental micrographs and multislice simulations suggests that the (110) surface reconstruction is similar to that derived by LEED.[4]

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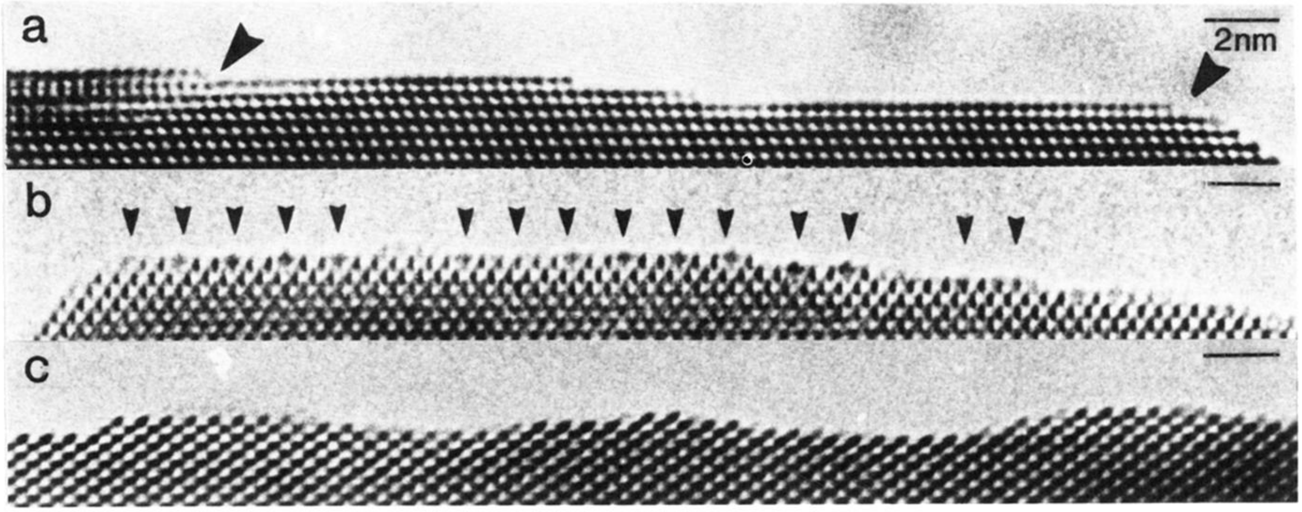

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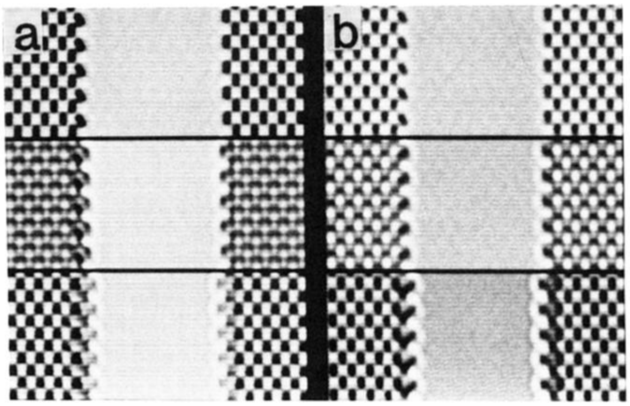

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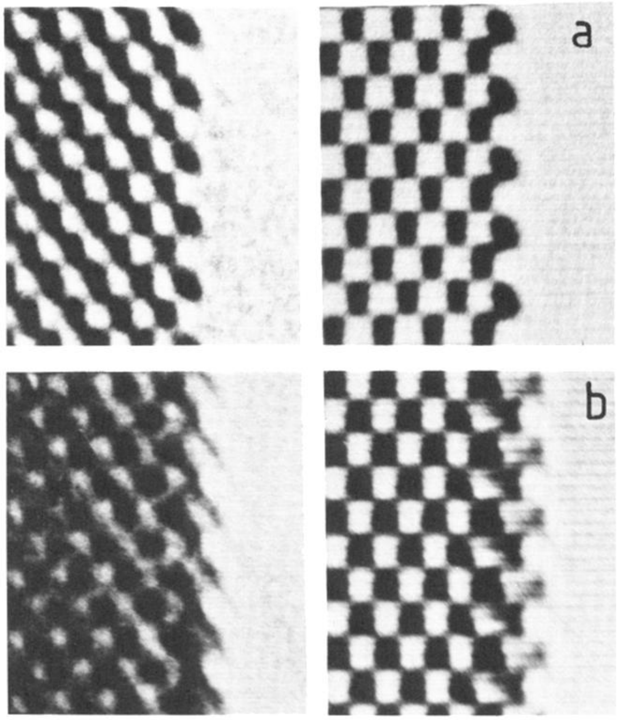

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